Supporting information for: Multireference Exciplex Binding Energies: Basis Set Convergence and Error

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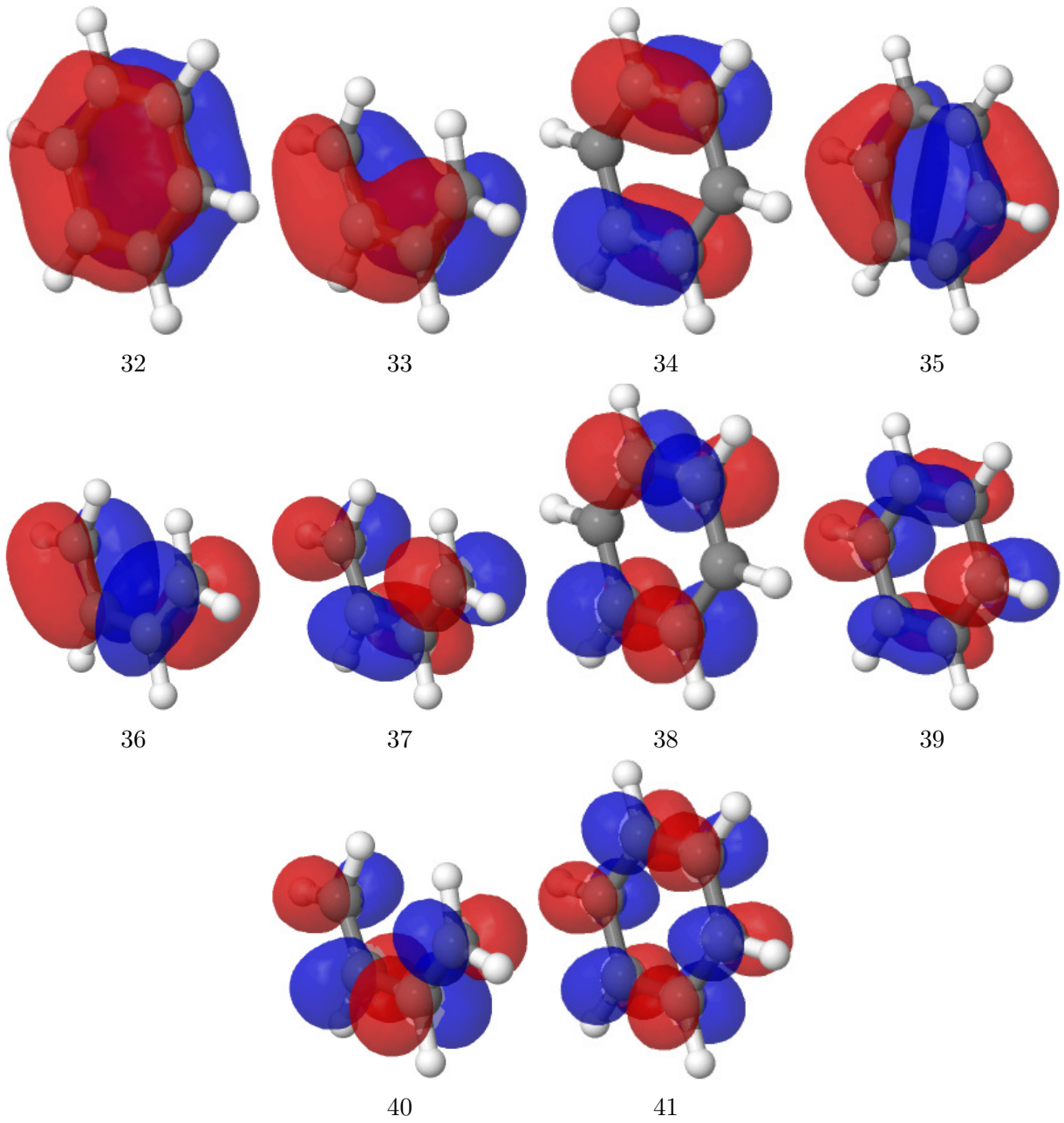

Figure S1: RHF starting orbitals for (BdBz)* CASSCF calculations with r_z = 10 Å. Only the monomer on which the orbital is localized is shown.

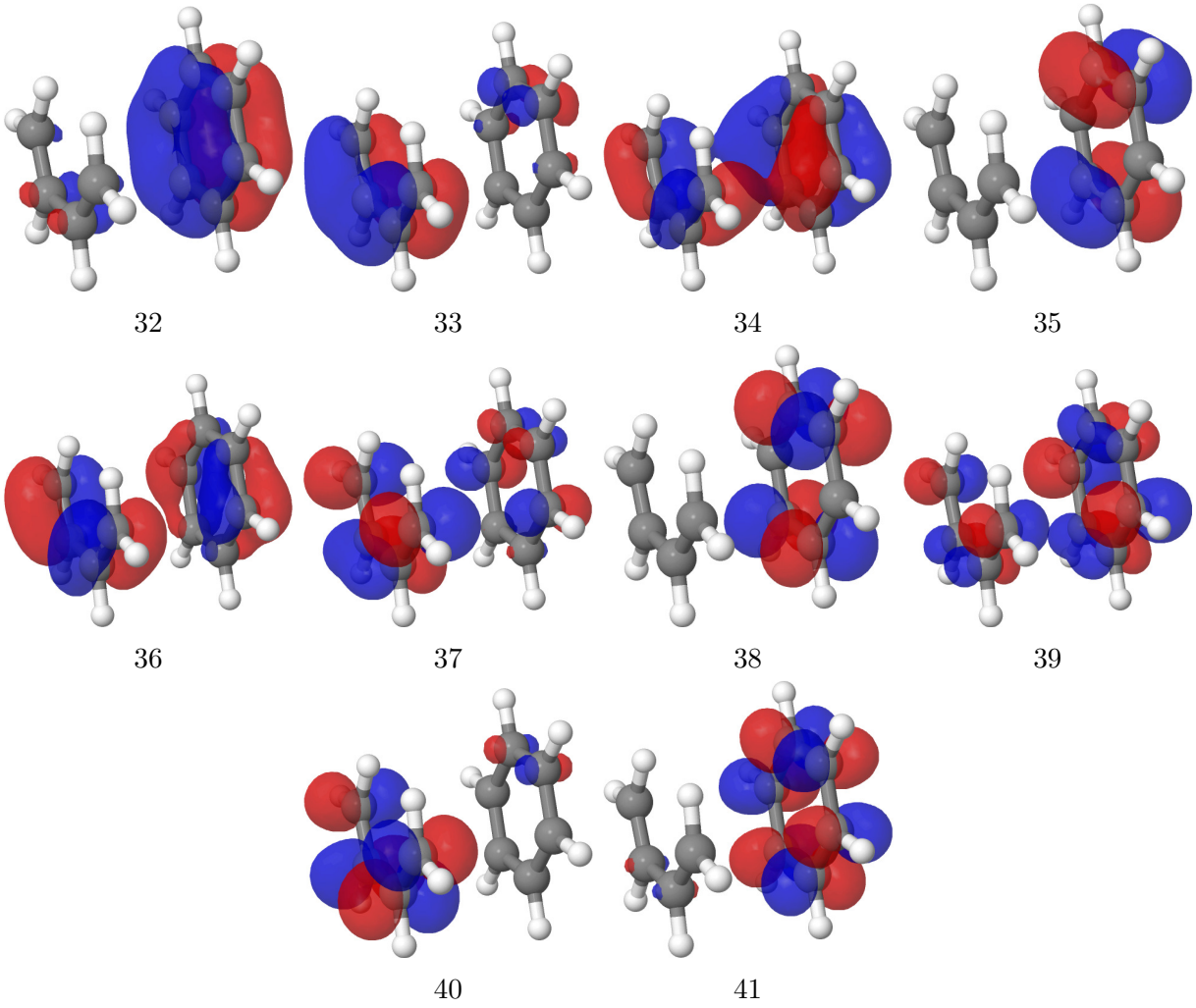

Figure S2: Starting orbitals for $(BdBz)^*$ with $r_z = r_0$.

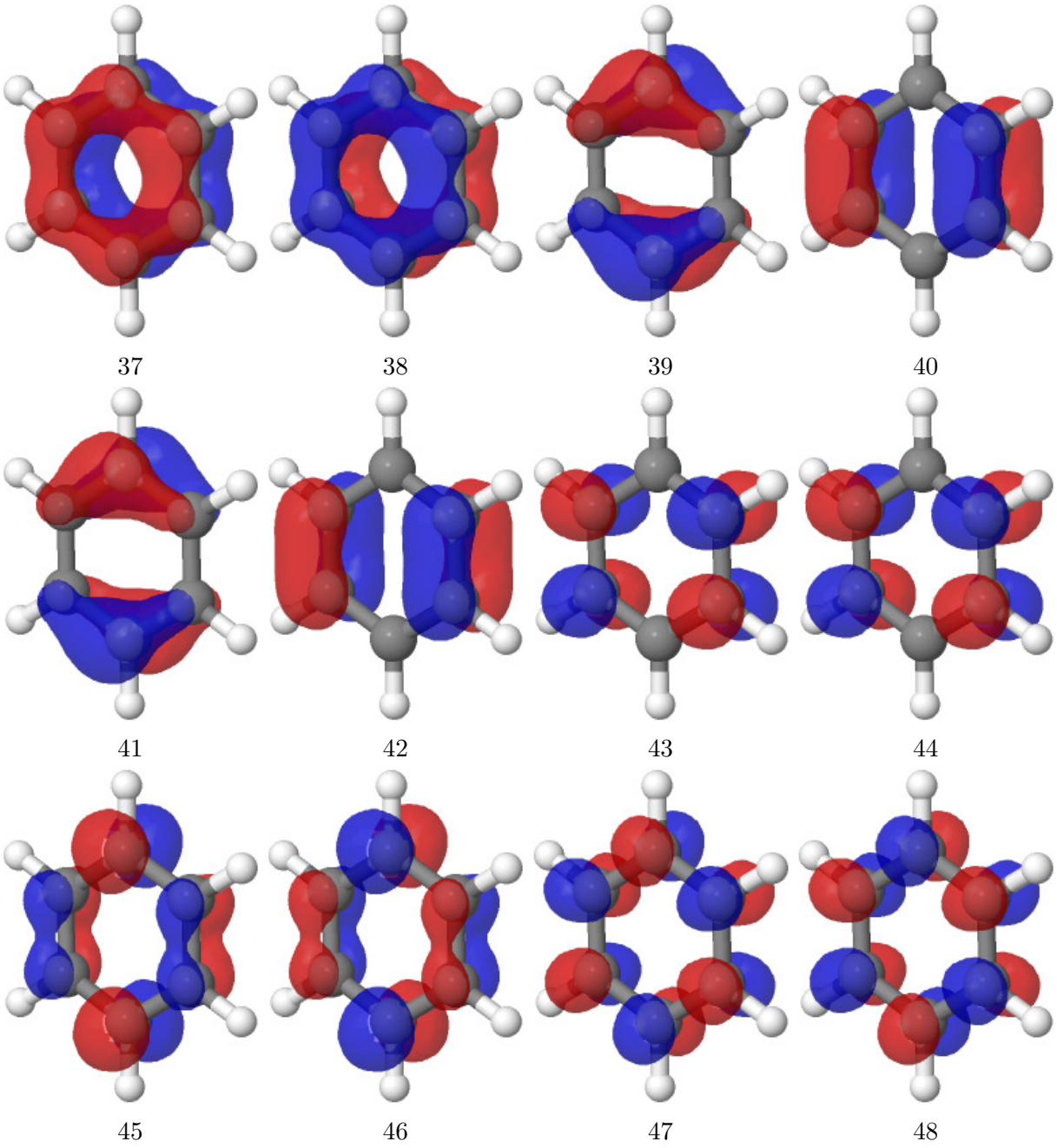

Figure S3: RHF starting orbitals for $(BzBz)^*$ CASSCF calculations with $r_z = 10$ Å.

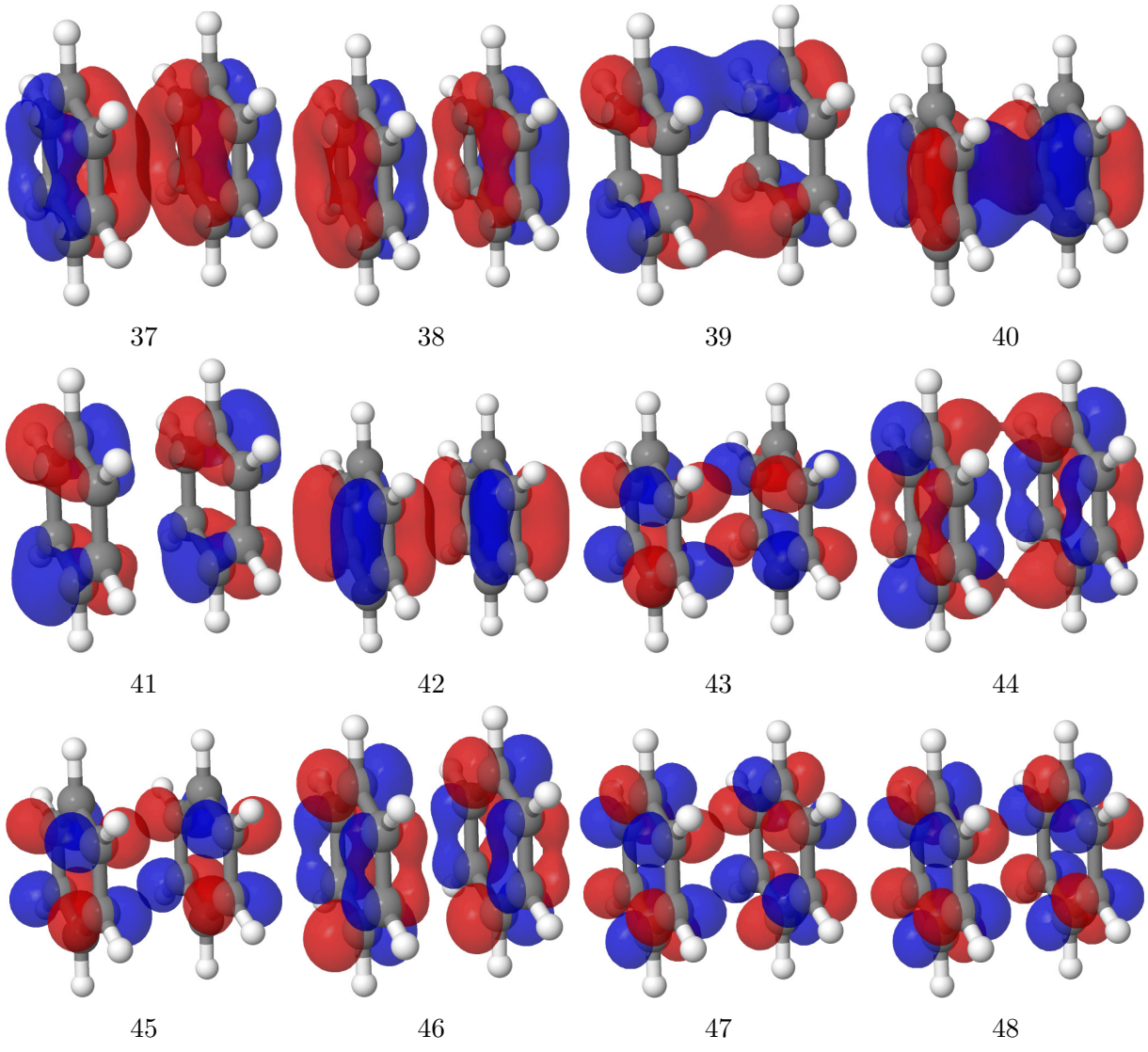

Figure S4: Starting orbitals for (BzBz)* CASSCF calculations with $r_z = r_0$.

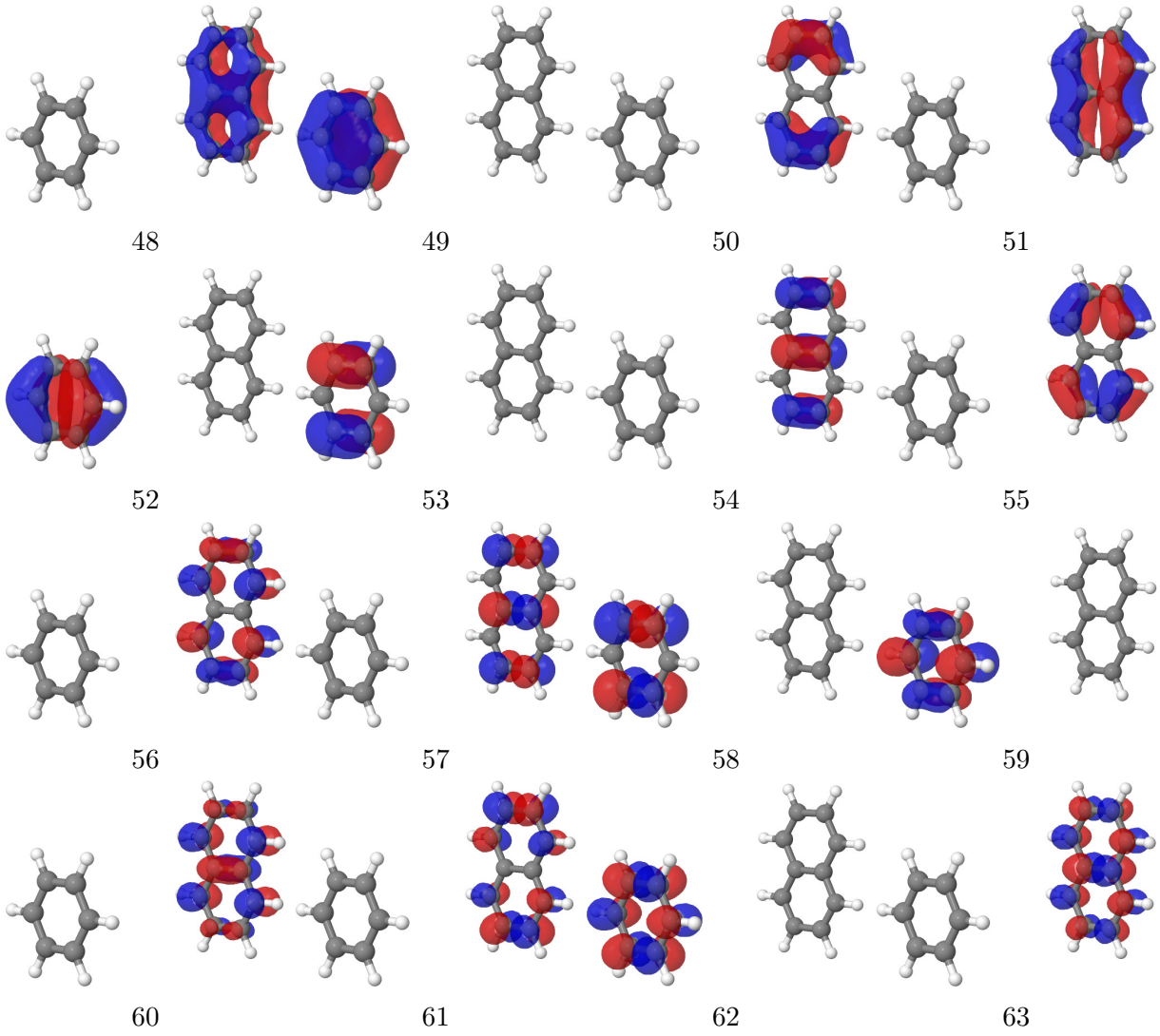

Figure S5: Starting orbitals for $(BzNa)^*$ with $r_z = 10$ Å.

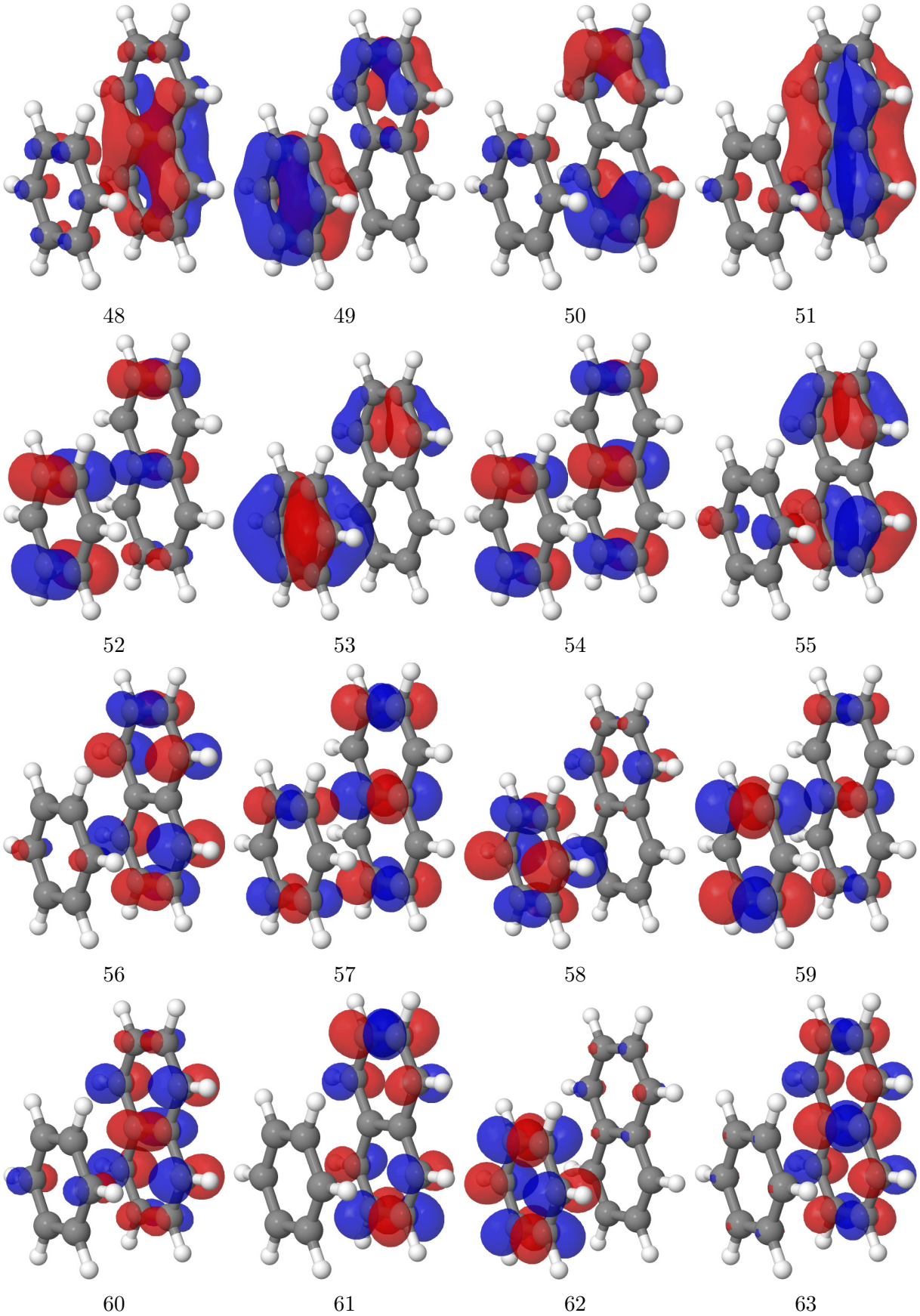

Figure S6: Starting orbitals for $(BzNa)^*$ CASSCF calculations with $r_z = r_0$.

Table S1: NEVPT2 binding energies for (BzNa)* in the S_1 state with different starting orbital types and M values. The aug-cc-pVTZ basis was used in all calculations.

Orbital Type	CASSCF M	CASCI/NEVPT2 M	$\lvert E_{Min}\rvert$ (kJ/mol)	$\lvert E_{Ref}\rvert$ (kJ/mol)	E_B (kJ/mol)
Local	500	1200	1619828.8	1619790.5	38.3
Local	800	1800	1619829.4	1619790.1	39.3
Local	1000	2250	1619829.4	1619790.1	39.3
Canonical	300	900	1619829.8	1619790.1	39.7
Canonical	500	1200	1619830.0	1619790.1	39.9
Canonical	800	1800	1619830.4	1619790.0	40.4
Canonical	1000	2250	1619830.4	1619790.1	40.3

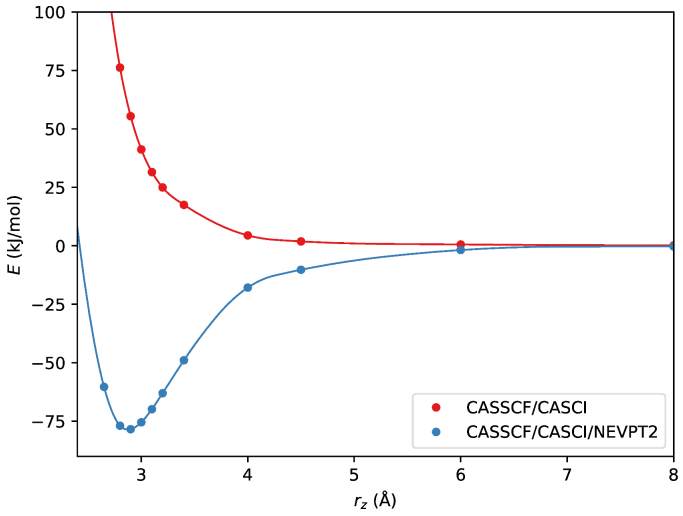

Figure S7: Energies for the benzene S_1 excimer computed using the aug-cc-pVTZ basis set. Lines have been added to guide the eye.

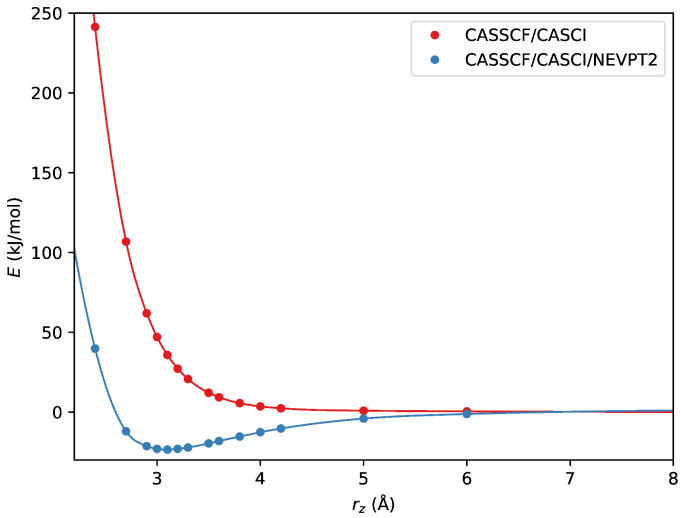

Figure S8: Energies for the *cis*-butadiene-benzene S_1 exciplex computed using the aug-cc-pVTZ basis set.

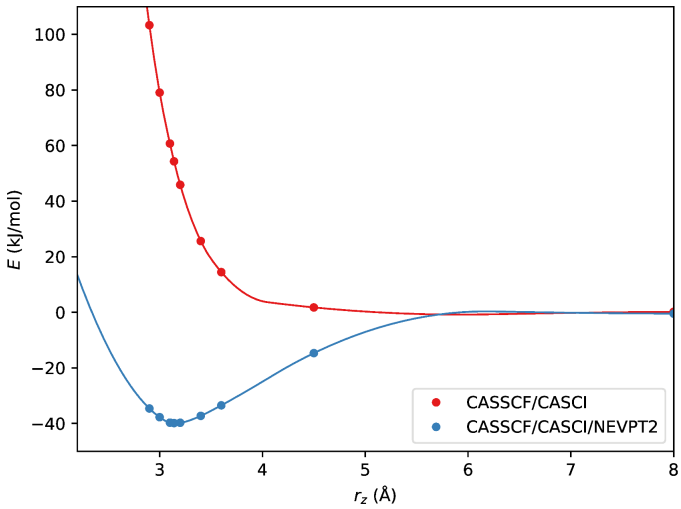

Figure S9: Energies for the benzene-naphthalene S_1 exciplex computed using the aug-cc-pVTZ basis set.

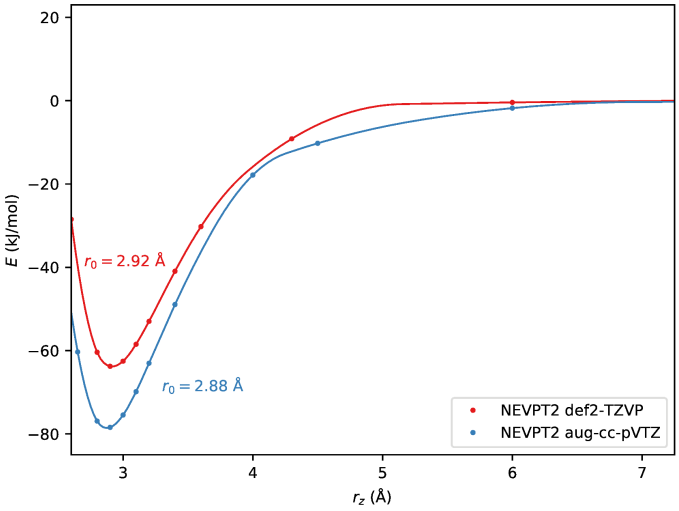

Figure S10: CASSCF/CASCI/NEVPT2 energies for the benzene S_1 excimer. Lines have been added to guide the eye.

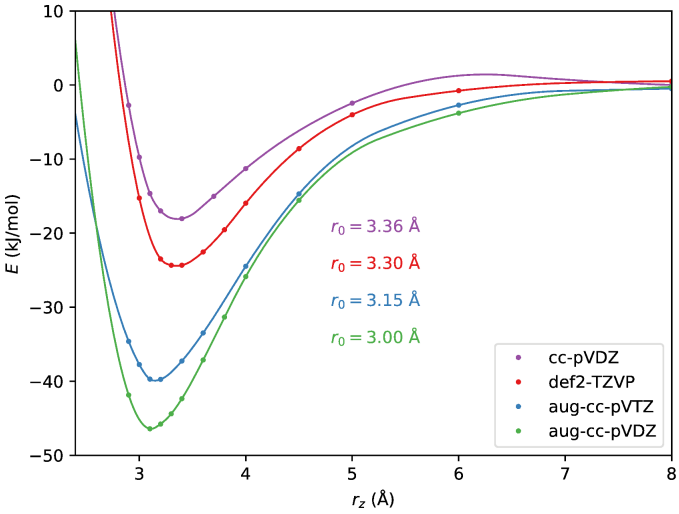

Figure S11: CASSCF/CASCI/NEVPT2 energies for the benzene-naphthalene S_1 exciplex.

Table S2: *Cis*-butadiene monomer coordinates

C	0.682701	1.753076	0.0
C	0.534938	0.428158	0.0
C	-0.726008	-0.321109	0.0
C	-1.960308	0.182633	0.0
H	1.665845	2.204406	0.0
H	-0.162196	2.431298	0.0
H	1.431809	-0.183803	0.0
H	-0.617379	-1.401412	0.0
H	-2.152068	1.248981	0.0
H	-2.826760	-0.465085	0.0

Table S3: Benzene monomer coordinates

C	0.0	1.390732	0.0
C	1.204409	0.695366	0.0
C	1.204409	-0.695366	0.0
C	0.0	-1.390732	0.0
C	-1.204409	-0.695366	0.0
C	-1.204409	0.695366	0.0
H	0.0	2.472794	0.0
H	2.141502	1.236397	0.0
H	2.141502	-1.236397	0.0
H	0.0	-2.472794	0.0
H	-2.141502	-1.236397	0.0
H	-2.141502	1.236397	0.0

Table S4: Naphthalene monomer coordinates

C	-1.545780	1.303980	0.0
C	-0.854520	2.487180	0.0
C	0.557100	2.487180	0.0
C	1.248350	1.303980	0.0
C	1.248350	-1.177190	0.0
C	0.557100	-2.360400	0.0
C	-0.854520	-2.360400	0.0
C	-1.545780	-1.177190	0.0
C	-0.862700	0.063390	0.0
C	0.565280	0.063390	0.0
H	-2.628710	1.302250	0.0
H	-1.388570	3.428150	0.0
H	1.091140	3.428150	0.0
H	2.331280	1.302250	0.0
H	2.331280	-1.175460	0.0
H	1.091140	-3.301370	0.0
H	-1.388570	-3.301370	0.0
H	-2.628710	-1.175460	0.0

Table S5: Absolute errors ($\Delta E_{B,Abs}$) and relative errors ($\Delta E_{B,Rel}$) for all E_B and $E_{B,CP}$ with respect to the E_{CBS} value extrapolated from the $\mathrm{N} = 3, 4$ basis sets of the largest family used for each exciplex.

	(BdBz)*				(BzBz)*				(BzNa)*			
	Uncorrected		CP-Corrected		Uncorrected		CP-Corrected		Uncorrected		CP-Corrected	
Basis Set	$\Delta E_{B,Abs}$	$\Delta E_{B,Rel}$	$\Delta E_{B,Abs}$	$\Delta E_{B,Rel}$	$\Delta E_{B,Abs}$	$\Delta E_{B,Rel}$	$\Delta E_{B,Abs}$	$\Delta E_{B,Rel}$	$\Delta E_{B,Abs}$	$\Delta E_{B,Rel}$	$\Delta E_{B,Abs}$	$\Delta E_{B,Rel}$
cc-pVDZ	2.4	0.21	19.1	1.72	6.6	0.12	35.7	0.63	1.16	0.06	25.6	1.33
cc-pVTZ	3.7	0.33	8.5	0.77	6.9	0.12	14.5	0.26	7.8	0.41	11.9	0.62
cc-pVQZ	1.1	0.10	4.1	0.37	2.7	0.05	6.1	0.11	1.09	0.06	6.0	0.31
jun-cc-pVDZ	0.3	0.03	13.4	1.21	4.2	0.08	27.7	0.49	5.3	0.27	18.0	0.94
jun-cc-pVTZ	9.1	0.82	4.1	0.37	19.3	0.34	7.8	0.14	18.3	0.95	5.4	0.28
jun-cc-pVQZ	3.8	0.34	1.5	0.14	6.7	0.12	2.6	0.05	5.5	0.29	2.3	0.12
jul-cc-pVDZ	16.1	1.45	7.3	0.66	23.4	0.41	12.9	0.23	22.4	1.2	8.2	0.43
jul-cc-pVTZ	11.7	1.05	1.7	0.16	20.0	0.37	4.3	0.08	18.3	0.95	3.7	0.19
jul-cc-pVQZ	3.46	0.31	1.0	0.09	6.2	0.11	1.8	0.03	–	–	–	–
aug-cc-pVDZ	17.8	1.61	3.6	0.32	28.7	0.51	11.23	0.20	25.2	1.31	7.3	0.38
aug-cc-pVTZ	12.4	1.12	1.8	0.16	21.9	0.39	3.6	0.06	20.3	1.06	3.2	0.17
aug-cc-pVQZ	4.4	0.40	0.75	0.07	–	–	–	–	–	–	–	–